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Reactivities of Oxygenated Cobalt Complexes

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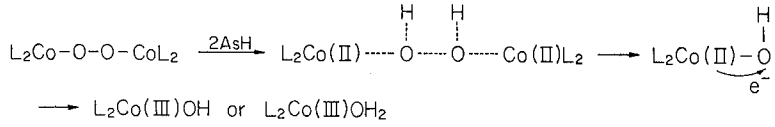
Oxygenated cobalt complexes, $[CoL_2]_2O_2$ [L: histidine(Hid), ornithine(Orn), diaminobutyric acid(DAB), diaminopropionic acid(DAP)] were oxidized to the cobaltic chelates with ascorbic acid (AsH) or benzoin and simultaneously hydrogen of AsH or benzoin was drawn. The reaction mechanism with ascorbic acid was proposed as follows:



The reactivity of $[CoL_2]_2O_2$ depended on the reversibility of oxygenation: Reversible complexes, ($[Co(Hid)_2]_2O_2$ and $[Co(Orn)_2]_2O_2$), were much reactive compared with the irreversible complexes, ($[Co(DAB)_2]_2O_2$ and $[Co(DAP)_2]_2O_2$), and the order of the reaction and the pH dependency in the oxidation of the formers and of the latters were also different with each other.

INTRODUCTION

There are many enzymatic reactions of interest, in which molecular oxygen participates and some metal ions play an important role as activator of oxygen molecules.[1] It has been suggested by Kobayashi[2] that the molecular oxygen may be excited to singlet state by coordinating to metal ion in enzyme, such as ferrous ion in pyrocatechase or hemoglobin and copper ion in ascorbate oxidase.

The oxygenated metal complexes may be very attractive as models of such enzymatic systems in the study of oxidation mechanisms of the oxygen molecule. Otsuka *et al.*[3] reported that the oxidation of t-butyl isocyanides (Bu ^{t}NC) was catalyzed by the oxygenated nickel complex (Ni (Bu ^{t}NC)$_2O_2$). Oxidations, by molecular oxygen, of triphenyl phosphine (Ph_3P) and hexyl isocyanide ($C_6H_{11}CN$) were accelerated in the presence of triphenyl phosphine chelates (M $(Ph_3P)_4$: M=Pd, Pt), and the existence of oxygenated complexes of palladium and platinum was confirmed as an intermediate in the oxidation process.[4]

Present authors reported that cobalt (II) chelates with ornithine, diaminobutyric acid and diaminopropionic acid combined with molecular oxygen to form binuclear cobalt complexes bridged by O_2, $L_2Co\text{-}O\text{-}O\text{-}CoL_2$ (L: ligand), similary in the case of cobalt (II) histidine chelate.[5] The histidine and ornithine chelates were reversibly oxygenated, but the diaminobutyric acid and diaminopropionic acid chelates, irreversibly.

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This work carried out to investigate how the reactivities of these oxygenated cobalt(II) complexes related to the thermodynamic stabilities of the complexes, the reversibilities of oxygenation and the electronic structures of coordinated molecular oxygen and central cobalt ions.

EXPERIMENTAL

Apparatus: Spectrophotometric measurements were made with a Shimadzu spectrophotometer QV-50 and a Shimadzu automatic recording spectrophotometer IV-50. A Hitachi-Horiba glass electrode pH meter was used for the pH measurements.

Materials: *Diaminobutyric acid (DAB) and diaminopropionic acid (DAP)* were obtained from Sigma Chemical Company, and histidine (Hid) and ornithine (Orn) were from Nakarai Chemical Co., Ltd. The other chemicals used were the reagent grade.

Procedure: Solution containing cobalt chelates ($2.63–5.26\times10^{-4}$M) is adjusted to a desired pH value; cobalt chelates are immediately oxygenated by this treatment. Four milliliters of the aliquot are placed in an absorption cell, 0.2 ml of ascorbic acid aqueous solution or 0.2 ml of benzoin dissolved in ethanol (each concentration: 5×10^{-3} M$\sim2\times10^{-2}$M) are added to the cell, and then the mixture is stirred for a few second. Absorbance of the solution at 390 mμ, which is the absorption maximum of characteristic band of the oxygenated cobalt complexes, is measured at appropriated time intervals. As buffers, KH_2PO_4-$NaHPO_4$ (5×10^{-3}M) and NH_3-NH_4Cl (5×10^{-3}M) were employed.

RESULTS AND DISCUSSION

Reaction of oxygenated cobalt complexes with ascorbic acid. When ascorbic acid was added to oxygenated cobalt histidine complex, $[Co(Hid)_2]_2O_2$, the absorption spectrum was deformed. As shown in Fig. 1, the new spectrum was quite different from the spectrum of the oxygenated complex[5] but it was approximately the same with that of cobalt(III) histidine chelate. The similar change of the absorption spectra occurred in the presence of benzoin. Although the spectrum did not completely agree with that of cobalt(III) histidine chelate, the shape and the intensity of the absorption were identical to those of cobalt(III) histidine chelate. This suggested that oxygenated cobalt histidine complex reacted also with benzoin.

The similar phenomena were observed in the cases of oxygenated cobalt complex of Orn, DAB and DAP, and this showed that those oxygenated complexes were also oxidized to the cobalt(III) chelates by addition of ascorbic acid or of benzoin.

Oxidation reactions of $[Co(Hid)_2]_2O_2$ and $[Co(Orn)_2]_2O_2$ with ascorbic acid followed the first order kinetics with respect to the concentration of the oxygenated complexes, whereas those of $[Co(DAB)_2]_2O_2$ and $[Co(DAP)_2]_2O_2$ obeyed neither the first, second and third order kinetics, as shown in Fig. 2.

The effect of the concentration of ascorbic acid on the oxidation of oxygenated

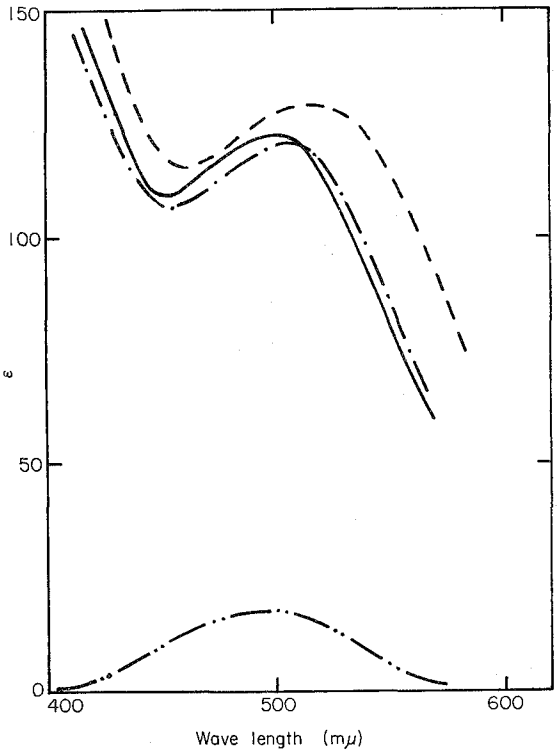


Fig. 1. Electronic absorption spectra of cobalt histidine chelates.

——: $[Co^{III}(Hid)_2]^+$; —·—: $[Co(Hid)_2]_2O_2$+ascorbic acid ;
– – –: $[Co(Hid)_2]_2O_2$+benzoin ; —··—: $[Co^{II}(Hid)_2]_2$; pH: 9.0

cobalt complexes was shown in Fig. 3 and Fig. 4. Oxidation rate of $[Co(Hid)_2]_2O_2$ decreased with the decrease in the concentration of ascorbic acid, and when molar ratio of ascorbic acid to $[Co(Hid)_2]_2O_2$ became lower than 2, the reaction did not follow the first order kinetics. Oxidation rates of $[Co(DAB)_2]_2O_2$ and $[Co(DAP)_2]_2O_2$, on the other hand, were scarecely influenced by the concentration of ascorbic acid, if the molar ratio was more than 2, although below the ratio 2, it decreased with decrease in the concentration of ascorbic acid. It was considered from these results that two moles of ascorbic acid probably reacted with one mole of oxygenated cobalt complexes.

The effect of pH on the oxidation of oxygenated complexes with ascorbic acid was shown in Fig. 5, which indicated that oxidation rate of $[Co(Hid)_2]_2O_2$ increased with the rise of pH, whereas the rates of $[Co(DAP)_2]_2O_2$ and $[Co(DAB)_2]_2O_2$ were almost independent of pH.

Thus, kinetic behaviors of reversible oxygenated complexes, $[Co(Hid)_2]_2O_2$ and $[Co(Orn)_2]_2O_2$, and of irreversible complexes, $[Co(DAB)_2]_2O_2$ and $[Co(DAP)_2]_2O_2$, were quite different, and it should be noted that the formers were much reactive than latters.

Ascorbic acid was also oxidized by oxygenated cobalt complexes: Absorption

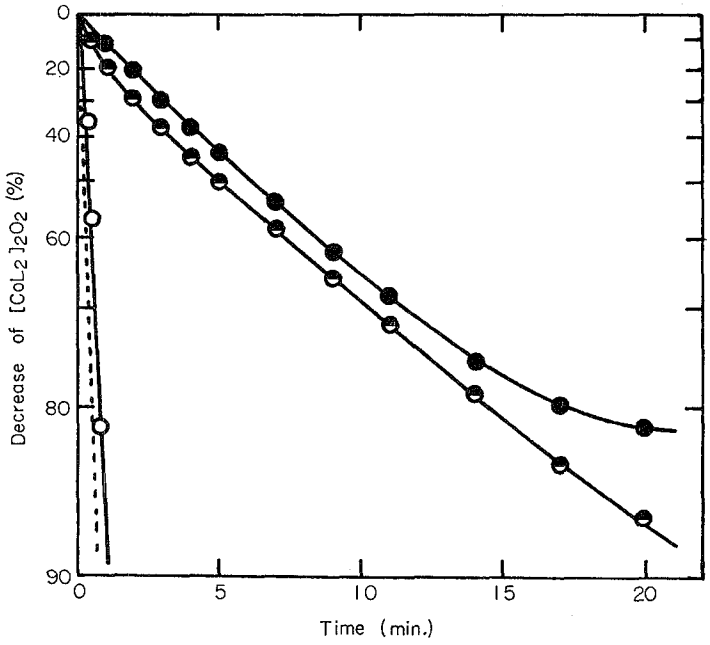


Fig. 2 Reactions of oxygenated cobalt complexes with ascorbic acid.

Oxygenated cobalt complex : 2.5×10^{-4}M ;
– – – : $[Co(Orn)_2]_2O_2$; —○— : $[Co(Hid)_2]_2O_2$;
—◐— : $[Co(DAB)_2]_2O_2$; —●— : $[Co(DAP)_2]_2O_2$;
Ascorbic acid : 5×10^{-4}M ; pH : 9.0 ; Temp.: 11～13°C

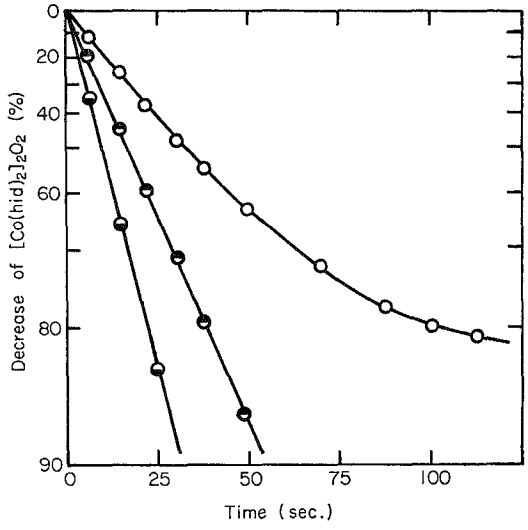


Fig. 3. Effect of concentration of ascorbic acid on oxidation of $[Co(Hid)_2]_2O_2$.

Ascorbic acid
—○— : 2.5×10^{-4}M
—◐— : 5.0×10^{-4}M
—◒— : 1.0×10^{-3}M

$[Co(Hid)_2]_2O_2$: 2.5×10^{-4}M
pH : 9.0
Temp. : 11～13°C

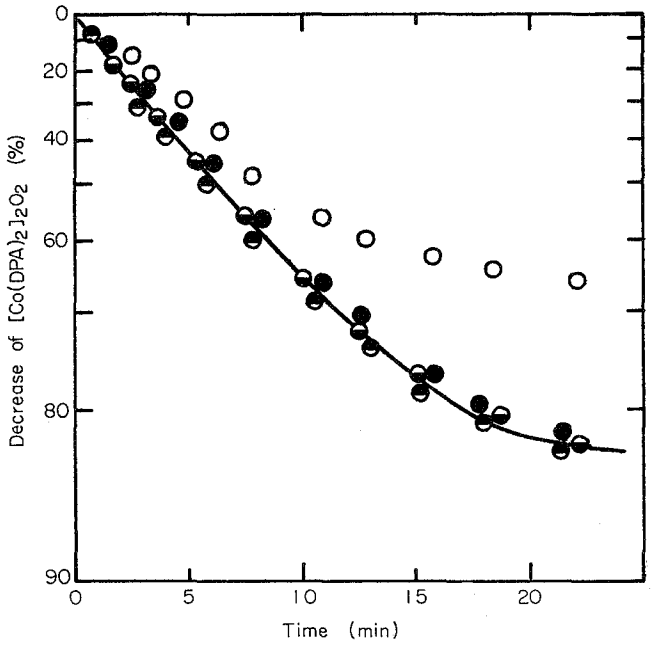


Fig. 4. Effect of concentration of ascorbic acid on oxidation of $[Co(DAP)_2]_2O_2$.

Ascorbic acid
○ : 2.5×10^{-4}M
◒ : 5.0×10^{-4}M
◒ : 1.0×10^{-3}M
● : 2.0×10^{-3}M

$[Co(DAP)_2]_2O_2$: 2.5×10^{-4}M
pH : 9.0
Temp. : 11～13°C

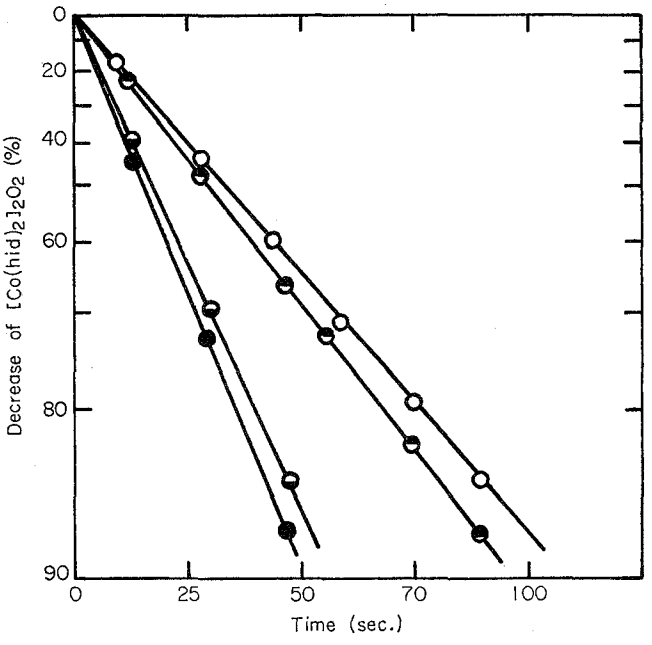
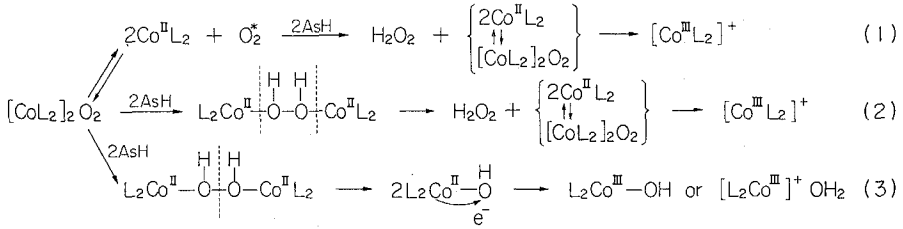


Fig. 5. Effect of pH on oxidation of $[Co(Hid)_2]_2O_2$ with ascorbic acid.

pH ; —○— : 7.0
—◒— : 8.0
—◒— : 9.0
—●— : 10.0

$[Co(Hid)_2]_2O_2$: 2.5×10^{-4}M
Ascorbic acid : 5.0×10^{-3}M
Temp. : 11～13°C

band characteristic for ascorbic acid at 265 mμ disappeared after the reaction. It is apparent at least that oxygenated cobalt complexes were oxidized to the cobalt (III) chelates by oxidation of ascorbic acid.



From the fact, three mechanisms may be considered as follows. The oxidations explained by the reaction mechanisms (1) and (2) are essentially the same with the oxidation with hydrogen peroxide, if the rate-determining step is oxidation of $[CoL_2]_2O_2$ with H_2O_2 but not drawing of hydrogen from ascorbic acid. However, Fig. 6 revealed that oxidation rate of $[CoL_2]_2O_2$ with hydrogen peroxide was minimum at pH 9.00, and the pH-dependency was different from that in the case of ascorbic acid. If drawing of hydrogen from ascorbic acid is the rate-determining step, oxidation of $[CoL_2]_2O_2$ with ascorbic acid must be slower than that with hydrogen peroxide. But the fact was inverse (see Fig. 5 and Fig. 6). Therefore, it may be unreasonable

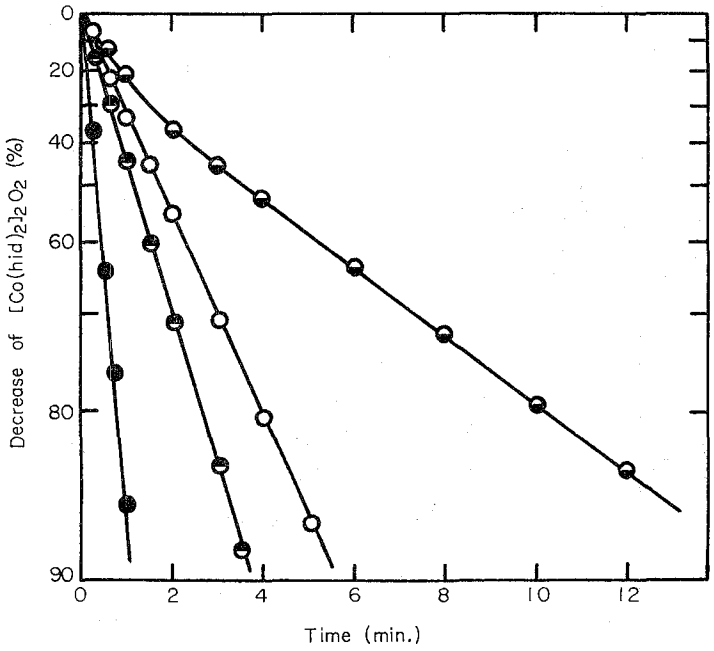


Fig. 6. Oxidation of $[Co(Hid)_2]_2O_2$ with hydrogen peroxide.

pH ; —○— : 7.0
—◐— : 8.0
—◒— : 9.0
—●— : 10.0

$[Co(Hid)_2]_2O_2$: 2.5×10^{-4}M
H_2O_2 : 5.0×10^{-4}M
Temp. : 11~13°C

to consider mechanisms (1) and (2) for oxidation reaction of $[CoL_2]_2O_2$ with ascorbic acid.

In mechanism (3), drawing of hydrogen from ascorbic acid by $[CoL_2]_2O_2$ may be a rate-determining, because unstable bond, $\begin{matrix} H & H \\ | & | \\ -O- & -O- \end{matrix}$, is rapidly cleaved, and the subsequent electrontransfer in the radical readily occur. The drawing must depend on the electron affinity of coordinated molecular oxygen, strictly, on the electron affinity of the two antibonding π-orbitals (π^*). As previously reported, coordinated molecular oxygen and central cobalt ions are in the states of O_2^{2-} and Co(III), respectively. Reversible oxygenated cobalt complex, $[Co(Hid)_2]_2O_2$ and $[Co(Orn)_2]_2O_2$, of course, can take a continuous state between O_2 and O_2^{2-}, because coordinated molecular oxygen, O_2^{2-}, must become O_2 state to be released as free molecular oxygen in deoxygenation process. Coordinated molecular oxygen near O_2 state may be the excited molecular oxygen, $^3\Sigma_g^-$, which easily draw hydrogen of ascorbic acid. On the other hand, in irreversively oxygenated complexes, $[Co(DAB)_2]_2O_2$ and $[Co(DAP)_2]_2O_2$, coordinated molecular oxygen, O_2^{2-}, hardly become O_2 state, in turn two π^*-orbitals of the molecular oxygen are always filled with four electrons, and therefore electron affinity of the coordinated molecular oxygen is very low. This concept can explain well the facts that oxidation rates of reversible oxygenated cobalt complexes with ascorbic acid are much larger than that of irreversible

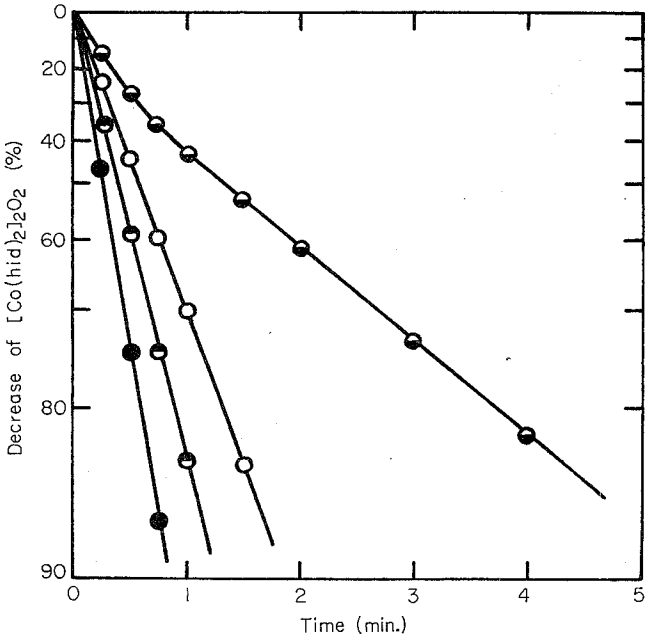


Fig. 7. Effect of pH on oxidation of $[Co(Hid)_2]_2O_2$ with benzoin.

pH ; —○— : 7.0
—◐— : 8.0
—◒— : 9.0
—●— : 10.0

$[Co(Hid)_2]_2O_2$: 2.5×10^{-4}M
Benzoin : 5×10^{-4}M
Temp. : 22~24°C

cobalt complexes, and in the same time, it may be reasonable to consider the mechanism (3) for the reaction between oxygenated cobalt complexes and ascorbic acid.

Reaction of oxygenated cobalt complexes with benzoin. Although it was expected that benzoin was oxidized to benzil through the reaction with oxygenated cobalt complexes, the spectrum of benzoin hardly change before and after the reaction. This may show that molecular oxygen of $[CoL_2]_2O_2$ drew hydrogen of hydroxide of benzoin to give benzoin anion.

When the molar ratio of benzoin to $[Co(Hid)_2]_2O_2$ was larger than 2, oxidation reaction obeyed the first order kinetics (Fig. 7), but not, bellow the ratio 2; two mole benzoin reacted with one mole $[Co(Hid)_2]_2O_2$.

Tendency of reactivities of oxygenated cobalt complexes with benzoin were the same that in the case of ascorbic acid: Reversible oxygenated complexes reacted more easily with benzoin than irreversible oxygenated complexes did, as shown in Fig. 8, and the oxidation rate increased in the following order;

$$[Co(DAP)_2]_2O_2 < [Co(DAB)_2]_2O_2 < [Co(Hid)_2]_2O_2 < [Co(Orn)_2]_2O_2$$

The pH-dependency, however, differently appeared: Oxidation rate of oxygenated cobalt complexes with benzoin showed a minimum (value) at pH 9.00, and the pH-dependency was almost the same with that in the oxidation with hydrogen peroxide. This suggested that the reaction of oxygenated cobalt complexes with benzoin probably

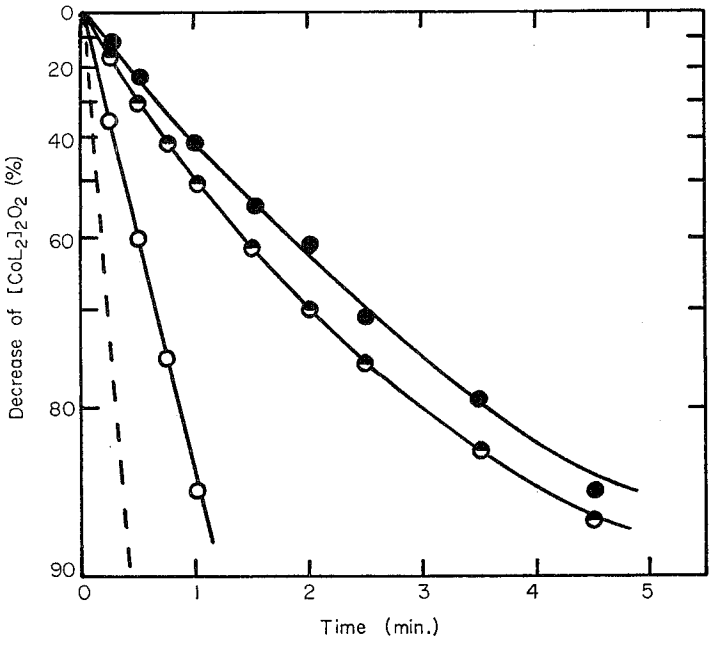


Fig. 8. Oxidation of oxygenated cobalt complexes with benzoin.

Oxygenated cobalt complex : 2.5×10^{-4}M ;
– – – : $[Co(Orn)_2]_2O_2$; —○— : $[Co(Hid)_2]_2O_2$;
—◐— : $[Co(DAB)_2]_2O_2$; —●— : $[Co(DAP)_2]_2O_2$;
Benzoin : 5×10^{-4}M ; pH : 9.0 ; Temp. : 22~24°C

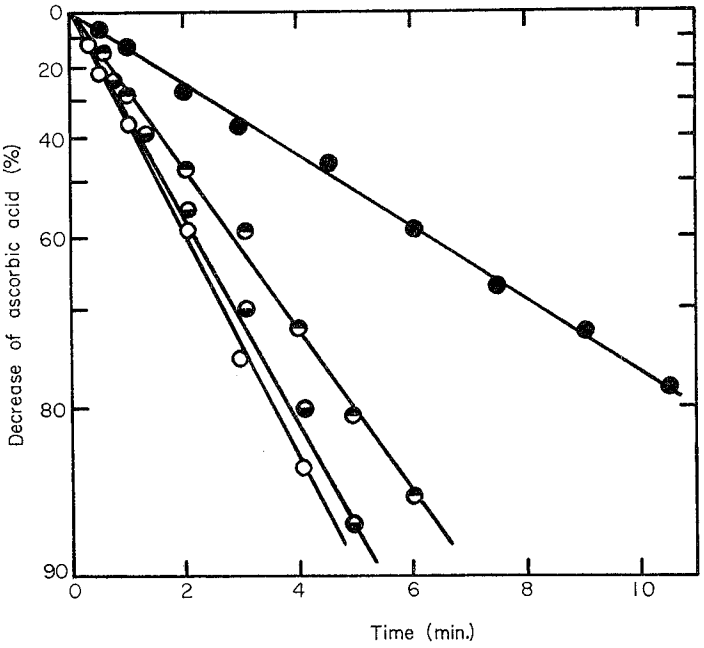


Fig. 9. Oxidation of ascorbic acid with oxygenated cobalt complexes.

Oxygenated cobalt complex : 5×10^{-5}M ;
—○— : $[Co(Orn)_2]_2O_2$; —◒— : $[Co(Hid)_2]_2O_2$;
—◓— : $[Co(DAB)_2]_2O_2$; —●— : $[Co(DAP)_2]_2O_2$;
Ascorbic acid : 5×10^{-5}M ; pH : 10.0 ; Temp. : 11～13°C

proceeded by mechanism (1) or (2), where ascorbic acid, of course, is replaced by benzoin.

Oxidation of ascorbic acid with $[CoL_2]_2O_2$. As described above, ascorbic acid was simultaneously oxidized in the oxidation process of oxygenated complexes. Oxidation rate of ascorbic acid with $[CoL_2]_2O_2$ increased with increase of pH value and also in the concentration of the complexes. The reaction followed the first order kinetics respect of the concentration of ascorbic acid at pH 10.0 (Fig. 9), but did not follow bellow pH 10.0 except in the case of $[Co(Hid)_2]_2O_2$. The acceleration order for oxidation of ascorbic acid increased in the following order;

$$[Co(DAP)_2]_2O_2 < [Co(DAB)_2]_2O_2 < [Co(Hid)_2]_2O_2 < [Co(Orn)_2]_2O_2$$

This was quite the same with the increasing order of oxidation of oxygenated cobalt complexes with ascorbic acid or benzoin.

Properties of oxygenated cobalt complexes were summarized in Table 1. The oxygenated complex, of which the thermodynamic stability, $[(CoL_2)_2O_2] / [CoL_2]^2[O_2]$ was lower, was more reactive, but the difference of the stability between $[Co(DAB)_2]_2O_2$ and $[Co(Hid)_2]_2O_2$ was not so large enough to explain a remarkable gap of reactivity observed between those complexes. And oxidation potential of cobalt in oxygenated complexes did not completely related to the reactivity, though

Table 1. Reactivity of Oxygenated Cobalt Complexes

$[CoL_2]_2O_2$	L=Orn	Hid	DAB	DAP
Stability (K*)	1.6×10^4	6.6×10^5	7.2×10^6	9.1×10^7
Co(III)/Co(II)	−0.15 V	−0.03 V	−0.27 V	−0.41 V
Reversibility**	rev.	rev.	irr.	irr.
Reactivity		$>$	$\gg$	$\geqslant$

* $K=\dfrac{[CoL_2]^2[O_2]^2}{[CoL_2]_2O_2}$

** Oxygenation-deoxygenation reversibility.

the reactivity decreased with the increase of the potential, except of $[Co(Orn)_2]_2O_2$. However, it should be noted that the remarkable gap of reactivity appeared between reversible oxygenated complexes and irreversible oxygenated complexes, namely, the reactivities of oxygenated cobalt complexes strongly depend on the oxygenation-deoxygenation reversibility, which was dynamic factor rather than static factors, such as thermodynamic stability and oxidation potential of the central cobalt ions.

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